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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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To cite this Article Kothandaraman, H. and Devi, M. Saroja(1994) 'Kinetics of Polymerization of 1-Octene with the Catalyst Systems $TiCl_4$ - $AlEt_3$ or $AlEt_2Br$ ', Journal of Macromolecular Science, Part A, 31: 4, 395 — 412

To link to this Article: DOI: 10.1080/10601329409351527

URL: <http://dx.doi.org/10.1080/10601329409351527>

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KINETICS OF POLYMERIZATION OF 1-OCTENE WITH THE CATALYST SYSTEMS $\text{TiCl}_4\text{-AlEt}_3$ OR AlEt_2Br

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ABSTRACT

Kinetic studies were performed on the polymerization of 1-octene with the heterogeneous Ziegler–Natta catalyst systems $\text{TiCl}_4\text{-AlEt}_3$ (I) and $\text{TiCl}_4\text{-AlEt}_2\text{Br}$ (II). The apparent activation energies determined from Arrhenius plots with catalyst systems I and II are 37.62 and 44.03 kJ/mol, respectively. The rate of polymerization was found to be proportional to the catalyst and monomer concentrations. A two-step coordinate anionic mechanism involving competitive adsorption between the monomer and the cocatalyst on the catalyst surface (Langmuir–Hinshelwood model) was proposed based on the dependence of the rate on the cocatalyst concentration. The polymers were characterized by IR, $^1\text{H-NMR}$, and $^{13}\text{C-NMR}$ spectroscopy.

INTRODUCTION

The first reports of the synthesis of polymers of higher α -olefins appeared simultaneously with reports of the synthesis of isotactic polypropylene [1, 2]. Conventional heterogeneous Ziegler–Natta catalysts are widely used for the polymerization of higher olefins under the same conditions as those used for propylene and 1-butene [3, 4]. Among the various α -olefins, 1-octene is the monomer of choice since other lower members like 1-hexene are low boiling and higher members like

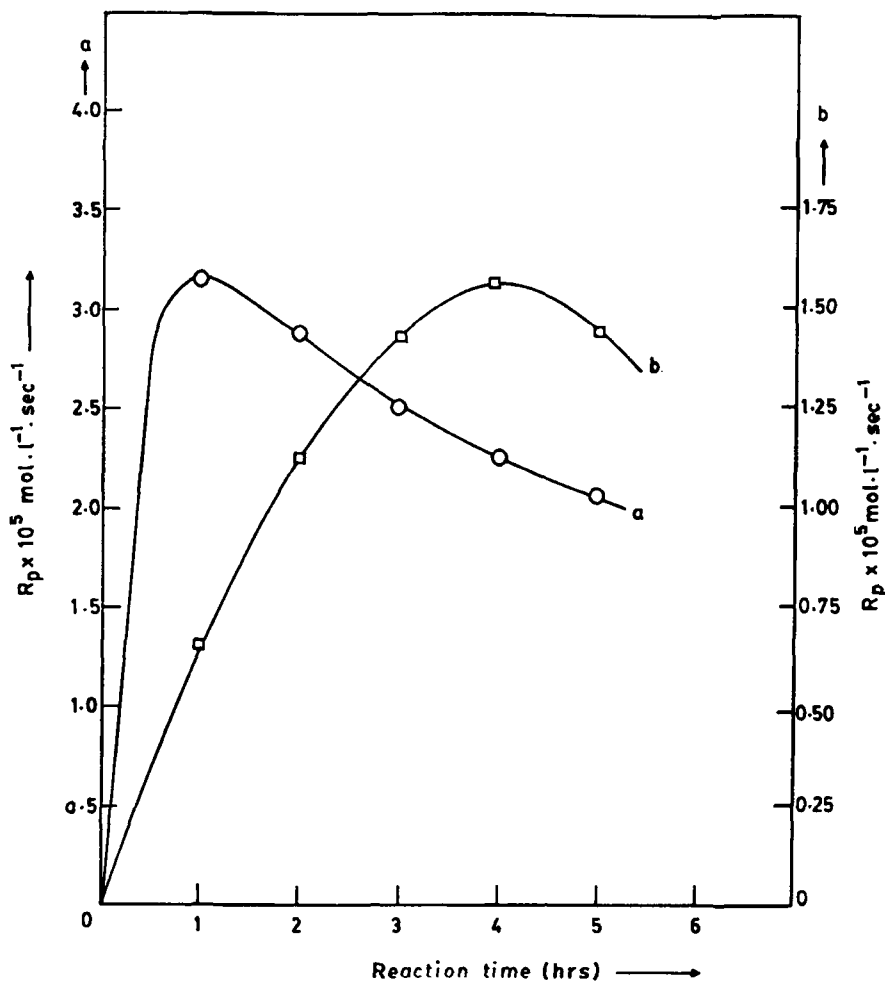


FIG. 1. Effect of the reaction time on the rate of polymerization of 1-octene with (a) catalyst I and (b) catalyst II.

1-decene are not very pure (due to contamination with the isomers). 1-Octene of 99% purity is available commercially. There have been many reports of the polymerization of 1-octene using a variety of Ziegler and other catalysts to produce polymers having both different stereospecificities and molecular weights. The kinetics of 1-octene polymerization, however, has been reported in only a few instances [5, 6]. Hence, considering the above facts and the low cost, ease of handling (being a liquid monomer), and high purity, it was proposed to investigate the kinetics and mechanism of polymerization of 1-octene with the Ziegler-Natta catalysts (as 1-octene is not polymerized readily with other types of initiators).

TABLE 1. Effect of Reaction Time on the Rate of Polymerization and the Molecular Weight of the Polymer^a

Reaction time, <i>t</i> , hours	$R_p \times 10^5 \text{ mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$		Molecular weight $\times 10^{-4}$	
	Catalyst I	Catalyst II	Catalyst I	Catalyst II
1	3.145	0.708	2.851	0.9904
2	2.875	1.125	4.248	1.6588
3	2.504	1.436	7.373	4.2965
4	2.249	1.573	9.062	6.8748
5	2.072	1.478	9.106	6.9045

^aPolymerization conditions: Aging time = 25 minutes, [1-octene] = 1 mol·L⁻¹, [TiCl₄] = 0.01 mol·L⁻¹, [aluminum alkyl] = 0.02 mol·L⁻¹, Al/Ti = 2.

EXPERIMENTAL

Materials

The solvents *n*-heptane (S.D. Fine Chemicals Ltd.) and ethanol (Devan and Company) were purified according to reported procedures [7]. 1-Octene (Sigma) was purified by refluxing over sodium for 5 hours, distilling, and storing over calcium hydride. TiCl₄ (Rideal, Germany) was used as received. AlEt₂Br and AlEt₃ were prepared by reported procedures [8] and their purities were established by estimating the amount of aluminum by EDTA titration after hydrolyzing known quantities of the aluminum alkyl with dilute HCl. Nitrogen (IOL, Madras) was purified by passing it through Fieser's solution, sulfuric acid, calcium chloride and finally a tube containing molecular sieves (3Å).

Polymerization

A two-necked round-bottomed flask fitted with a rubber septum and a nitrogen inlet outlet tube was used as the polymerization reactor. The reactor was purged with nitrogen for a short time, and the nitrogen inlet-outlet tube was closed. Required amounts of the solvent, catalyst, and cocatalyst (AlEt₃ or AlEt₂Br) were injected through the septum in the same order, allowed to age, the required amount of monomer was added, and the reactor was kept in a specially fabricated constant temperature bath which can accommodate six reactors at a time with magnetic stirring in all the reactors individually. After the specified reaction time, the reaction was arrested by addition of ethanol containing 5% hydrochloric acid. The contents of the flask were then poured into a large excess of acidified ethanol and left

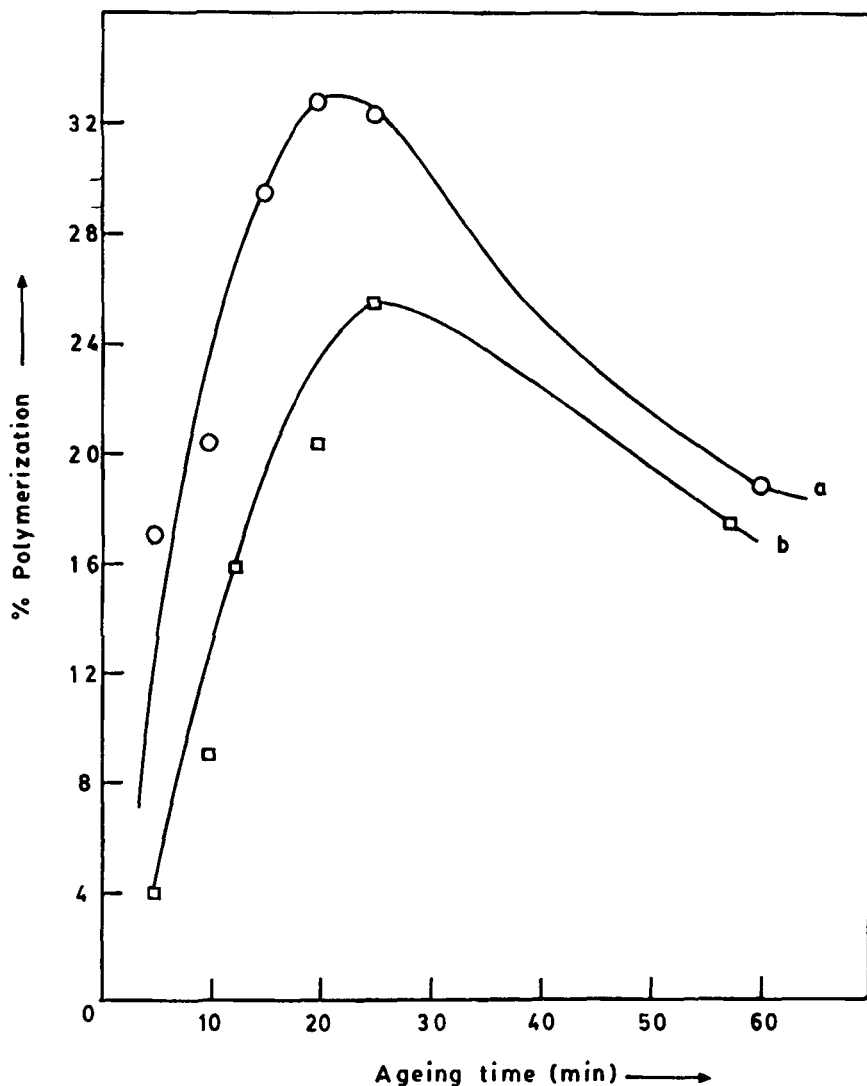


FIG. 2. Effect of the aging time on the percentage polymerization of 1-octene with (a) catalyst I and (b) catalyst II

overnight for the polymer to settle down. The polymer was washed with ethanol, dried in a vacuum oven at 50°C for 24 hours, and weighed.

Characterization of the Polymers

The intrinsic viscosities of the polymers were measured in cyclohexane at $30 \pm 0.1^{\circ}\text{C}$ using an Ubbelohde viscometer. Extrapolation methods of Huggins [9] and Kraemer [10] were used for evaluating the intrinsic viscosities. The molecular weight was calculated using the formula [11]

TABLE 2. Effect of the Aging Time on the Percentage Polymerization and the Molecular Weight of the Polymer^a

Aging time, minutes	Percentage polymerization		Molecular weight $\times 10^{-4}$	
	Catalyst I	Catalyst II	Catalyst I	Catalyst II
5	17.2	3.96	3.655	1.625
10	20.3	9.19	3.841	2.599
15	29.8	15.87	4.755	3.701
20	33.1	20.38	6.079	4.814
25	32.2	25.50	8.536	6.505
60	18.5	17.51	6.948	5.150

^aPolymerization reaction time = 5 hours. Other conditions as in Table 1.

$$[\eta] = 5.75 \times 10^{-3} M^{0.78}$$

The polymers were characterized by IR, ¹H-NMR, and ¹³C-NMR spectroscopy. The IR spectra of the polymers were measured using a Perkin-Elmer 781 model in chloroform. The ¹H-NMR spectra of the polymer samples were run on a Varian EM 390-90 MHz instrument at 27°C using CDCl₃ as the solvent. The ¹³C-NMR spectra (¹H decoupled) of the polymer samples were run on a Jeol JNM 400 MHz instrument at 27°C operating at 100.4 MHz. CDCl₃ and TMS were used as the solvent and the internal standard, respectively. The number of scans for all the spectra were in the 5000 range. The delay between the pulses was 1.68 seconds, and the acquisition time was 0.65 seconds. The quantity of isotactic polymer was determined by identifying the signal characteristic of the isotactic sequence and by the cutting-weighing method.

TABLE 3. Effect of the Monomer Concentration on the Rate of Polymerization and the Molecular Weight of the Polymer^a

Monomer concentration, [M] · mol · L ⁻¹	$R_p \times 10^5 \text{ mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$		Molecular weight $\times 10^{-4}$	
	Catalyst I	Catalyst II	Catalyst I	Catalyst II
0.5	0.962	1.154	5.143	3.193
1.0	1.973	1.579	8.858	6.808
2.0	2.745	2.548	11.539	12.462
3.0	3.451	3.601	14.871	19.069

^aPolymerization conditions as in Table 2.

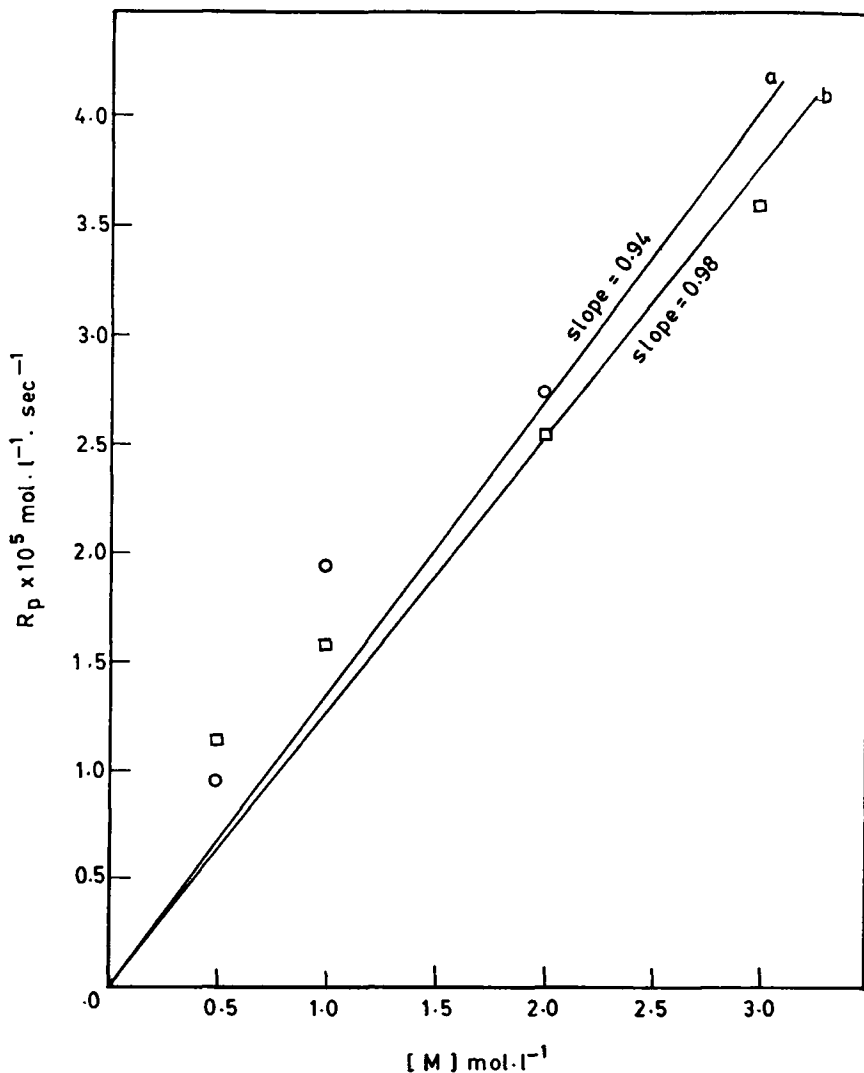


FIG. 3. Effect of the monomer concentration on the rate of polymerization of 1-octene with (a) catalyst I and (b) catalyst II.

RESULTS AND DISCUSSION

Kinetic Behavior of the Polymerization of 1-Octene

The kinetic behavior of the polymerization of 1-octene with the $\text{TiCl}_4\text{-AlEt}_3$ (I) and the $\text{TiCl}_4\text{-AlEt}_2\text{Br}$ (II) catalyst systems in heptane and at 40°C has been studied.

The effect of the reaction time on the rate of polymerization was studied at 40°C . The results are shown in Fig. 1 (Table 1). It is seen from Fig. 1 that the rate reached a maximum value within 1 hour with the catalyst system I, and with the

TABLE 4. Effect of the Catalyst Concentration on the Rate of Polymerization and the Molecular Weight of the Polymer^a

TiCl ₄ concentration × 10 ² mol·L ⁻¹	$R_p \times 10^5 \text{ mol}\cdot\text{L}^{-1}\cdot\text{s}^{-1}$		Molecular weight × 10 ⁻⁴	
	Catalyst I	Catalyst II	Catalyst I	Catalyst II
0.1	0.4132	0.6168	2.150	4.044
1.0	1.8509	1.2903	8.556	6.363
1.5	2.0850	1.8860	7.184	5.894
2.5	3.3945	2.9730	4.362	4.924

^aPolymerization conditions as in Table 2.

catalyst system II the rate increased slowly for 4 hours and then decreased. The maximum in the rate observed may be due to the completion of active center formation. The decrease in the rate after a maximum may occur as a result of a decrease in monomer concentration at longer polymerization times and deactivation of active centers. The molecular weights of the polymers increased with increasing time with both the catalyst systems (Table 1).

Aging time was varied from 5 to 60 minutes. After the addition of the cocatalyst (aluminum alkyl) to the TiCl₄ solution, a brown-black precipitate formed. Maximum conversion was observed with the catalyst system aged for 25 minutes with catalyst II and 20 minutes with catalyst I (Fig. 2) which can be explained as due to the slow formation of active centers. The decrease in rate with longer aging times may be due to the decay of the active centers on prolonged aging due to the further reduction of the transition metals to lower valent states which are inactive for olefin polymerization. In the present study an optimum aging time of 25 minutes was allowed for all polymerizations. The molecular weight of the polymers increased with increasing aging time, reached a maximum, and then decreased (Table 2).

Table 3 illustrates the details of the effect of catalyst concentration on the rate of polymerization and the molecular weight of the polymer. From Fig. 3 it is obvious that the order of the reaction with respect to the monomer is 1 for the two catalyst systems under study. The molecular weight of poly(1-octene) increased with increasing monomer concentration (Table 3), precluding chain transfer to the monomer.

The results of the effect of catalyst concentration on the rate of polymerization and the molecular weight of the polymer are given in Table 4. A first-order dependence of the rate of polymerization on the catalyst concentration was observed (Fig. 4) in the polymerization of 1-octene with both catalyst systems studied. The decrease in molecular weight with increasing catalyst concentration indicated chain transfer to the catalyst. However, at lower catalyst concentrations a reversible trend was observed. The cocatalyst-to-catalyst ratio was varied by keeping the amount of TiCl₄ constant and varying the amount of aluminum alkyl; Table 5 gives the details. From Fig. 5 it can be seen that as the ratio is increased, in the beginning there is a gradual increase in the percentage of polymerization, then a maximum, and finally the percentage polymerization decreases. This shows that the combination of TiCl₄

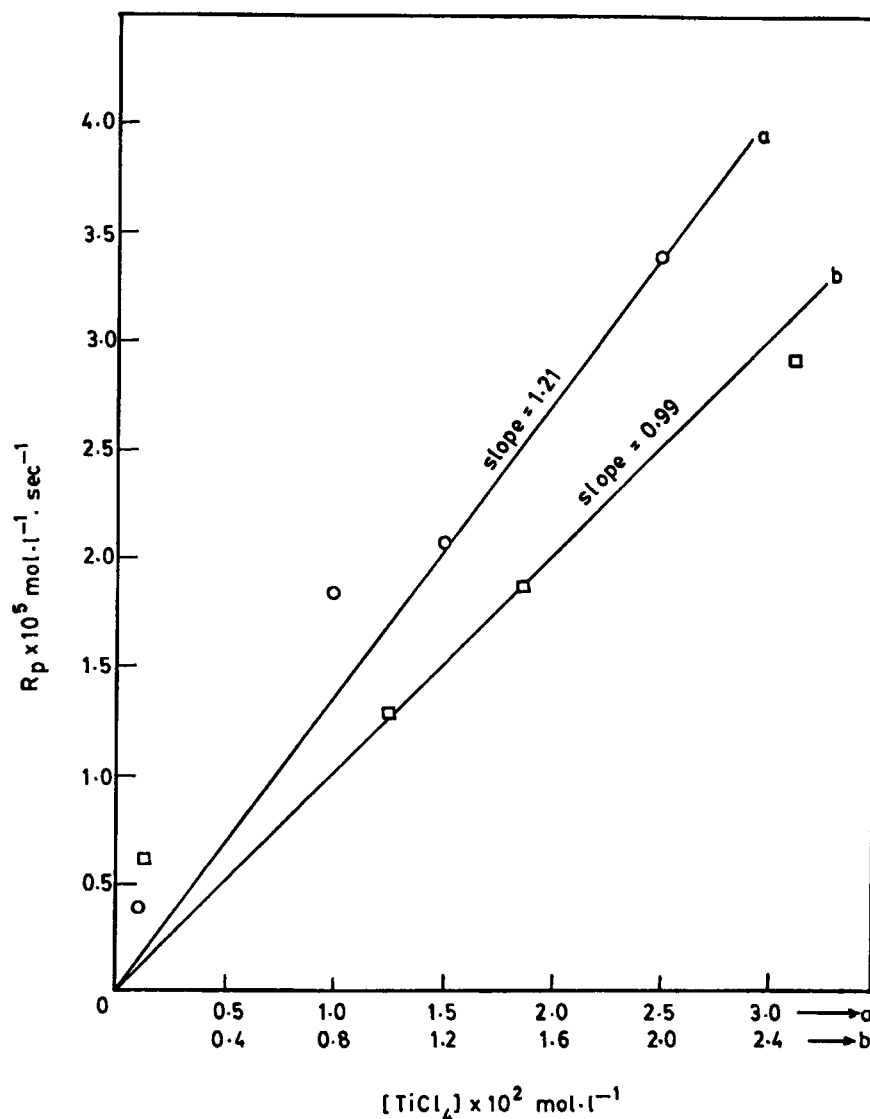


FIG. 4. Effect of the catalyst concentration on the rate of polymerization of 1-octene with (a) catalyst I and (b) catalyst II.

with these alkyls is most active at a particular $[\text{Al}]/[\text{Ti}]$ ratio. Only at a particular ratio is a maximum yield obtained. This may be due to the fact that at this ratio the maximum number of active sites is formed which is capable of propagating the polymer chain. These results can also be interpreted on the basis of alkyl concentration. Dependence of the rate on the alkyl concentration can be explained based on the Langmuir-Hinshelwood mechanism. Straight lines are obtained when Langmuir-Hinshelwood plots are drawn (Table 6, Fig. 6). The polymerization tempera-

TABLE 5. Effect of the Al/Ti Ratio on the Percentage Polymerization and the Molecular Weight of the Polymer^a

Al/Ti ratio	Percentage polymerization		Molecular weight $\times 10^{-4}$	
	Catalyst I	Catalyst II	Catalyst I	Catalyst II
1.0	22.34	21.32	3.248	3.664
1.5	29.60	24.18	6.951	5.586
2.0	33.55	26.97	8.843	6.419
2.5	39.43	30.41	6.510	5.041
3.0	36.76	25.71	4.968	3.041
5.0	29.24	21.75	2.644	1.124

^aPolymerization conditions as in Table 2.

ture was varied between 35 and 60°C. Details are furnished in Table 7. It is obvious from Table 7 that the rate as well as the molecular weight of the polymer decreased with increasing temperature. The activation energies were determined from the slope of the Arrhenius plot to be 37.62 and 44.03 kJ/mol for catalyst systems I and II, respectively. These values are consistent with those reported for coordinate anionic polymerizations of olefins [12–15].

Mechanism

Based on the above experimental results, a two-step coordinate anionic mechanism involving competitive adsorption of both monomer and the aluminum alkyl on the solid surface (Langmuir–Hinshelwood model) is proposed.

The rate of polymerization R_p is given by

$$R_p = k_p c^* \Theta_A \Theta_M \quad (1)$$

where k_p = rate constant for propagation
 c^* = concentration of active centers

$$\Theta_A = \frac{K_A[A]}{1 + K_M[M] + K_A[A]}$$

$$\Theta_M = \frac{K_M[M]}{1 + K_M[M] + K_A[A]}$$

(fractions of the surface covered by the alkyl and the monomer, respectively).

Therefore,

$$R_p = \frac{k_p c^* K_A K_M [A] [M]}{(1 + K_M[M] + K_A[A])^2} \quad (2)$$

From Eq. (2) it is seen that

$$R_p \propto [M][\text{cat}]$$

since $c^* \propto [\text{cat}]$.

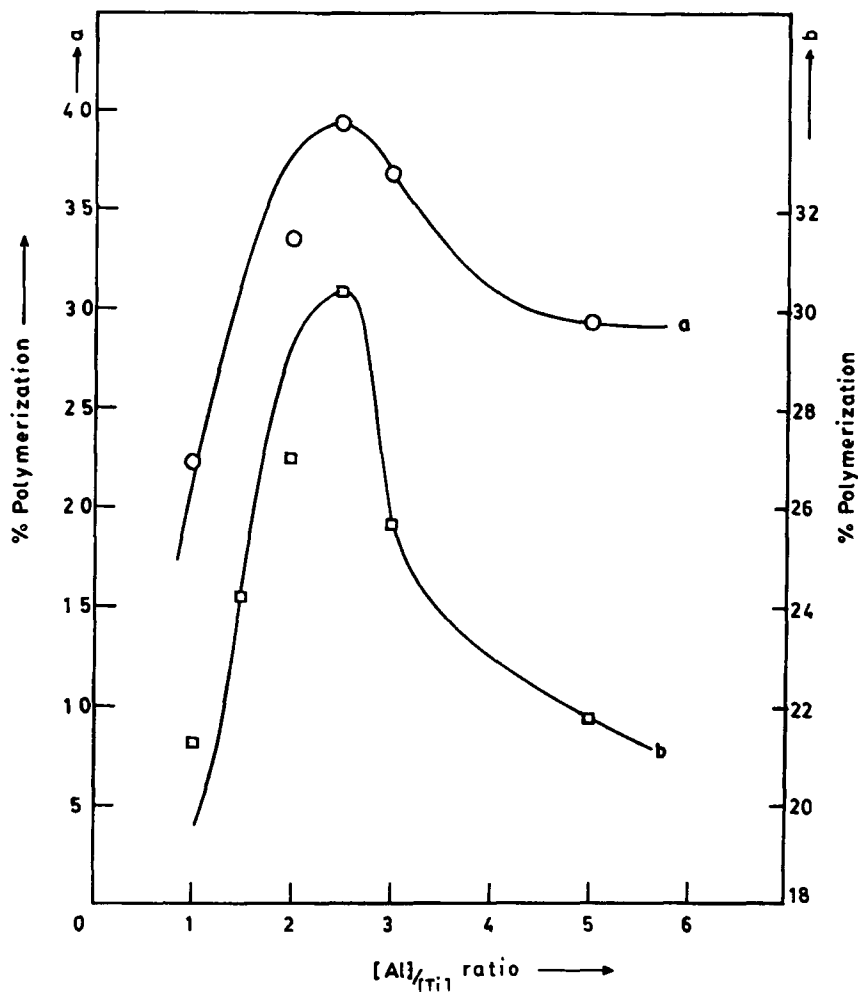


FIG. 5. Effect of the Al/Ti ratio on the percentage of the polymerization of 1-octene with (a) catalyst I and (b) catalyst II.

Under conditions where the concentration of the monomer is constant and the concentration of the aluminum alkyl is sufficiently large, $K_A[A] \gg K_M[M]$ and Eq. (2) becomes

$$R_p = \frac{k_p K_A c^* [A]}{(1 + K_A [A])^2} \quad (3)$$

Figure 7 shows plots of $([A]/R_p)^{1/2}$ against $[A]$. Linear plots were obtained.

Polymer Characterization

IR Spectroscopy

The IR spectrum of poly(1-octene) prepared with catalyst I is shown in Fig. 8. The C-H stretching and bending vibrations of the methyl group are seen at 2850

TABLE 6. Effect of the Alkyl Aluminum Concentration on the Rate of Polymerization^a

Alkyl aluminum concentration $\times 10^2 \text{ mol} \cdot \text{L}^{-1}$	$R_p \times 10^5 \text{ mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$		$([\text{Alkyl aluminum}]/R_p)^{1/2} \cdot \text{s}^{1/2}$	
	Catalyst I	Catalyst II	Catalyst I	Catalyst II
1.0	1.241	1.184	28.40	29.1
1.5	1.644	1.343	30.20	33.4
2.0	1.864	1.498	32.80	36.5
2.5	2.190	1.689	33.79	38.5
3.0	2.042	1.428	38.30	45.8
5.0	1.624	1.208	55.50	64.3

^aPolymerization conditions as in Table 2.

and 1460 cm^{-1} , respectively. The methylene groups showed absorptions at 2850 , 1370 , and 720 cm^{-1} due to C—H stretching, bending, and deformation, respectively. The disappearance of the bands at 1395 and 1640 cm^{-1} due to C—H stretching of the vinylic group and C=C stretching, respectively, indicates the formation of poly(1-octene).

¹H-NMR Spectroscopy

The ¹H-NMR spectrum of poly(1-octene) is shown in Fig. 9. The triplet appearing at 0.85 ppm is due to the methyl group, and the singlet at 1.25 ppm is attributed to the methylene groups. The backbone methine gave a signal at 1.75 ppm . The absence of signals at $5\text{--}6 \text{ ppm}$ shows that polymerization has proceeded.

¹³C-NMR Spectroscopy

¹H-NMR spectroscopy cannot be used as a tool for determining the tacticity of poly(1-octene) because of the overlapping of the proton signals in a narrow range ($0.6\text{--}1.8 \text{ ppm}$). Hence, ¹H-decoupled ¹³C-NMR has been used for the identification as well as the determination of tacticity. The ¹H-decoupled ¹³C-NMR spectrum of poly(1-octene) (Fig. 10) shows eight signals due to eight different carbons.

$\text{C}^1 = 40.29 \text{ ppm}$	$\text{C}^5 = 29.98 \text{ ppm}$
$\text{C}^2 = 32.40 \text{ ppm}$	$\text{C}^6 = 32.07 \text{ ppm}$
$\text{C}^3 = 35.02 \text{ ppm}$	$\text{C}^7 = 22.80 \text{ ppm}$
$\text{C}^4 = 26.37 \text{ ppm}$	$\text{C}^8 = 14.15 \text{ ppm}$

From an earlier report by Asakura et al. [16] and using the RIS (rotational isomeric state) model [17], the signal appearing at the low field with the pentad sequence was found to be due to the isotactic polymer. Since the intensity of the carbon signal denotes the content of stereochemically similarly positioned carbons, a low field C^3 signal was employed for calculating the isotactic content (Fig. 11a–b) by the cutting-weighting method. By this method the $\text{TiCl}_4\text{--AlEt}_3$ and $\text{TiCl}_4\text{--AlEt}_2\text{Br}$ catalyst systems were found to produce 36 and 43% isotactic polymer, respectively.

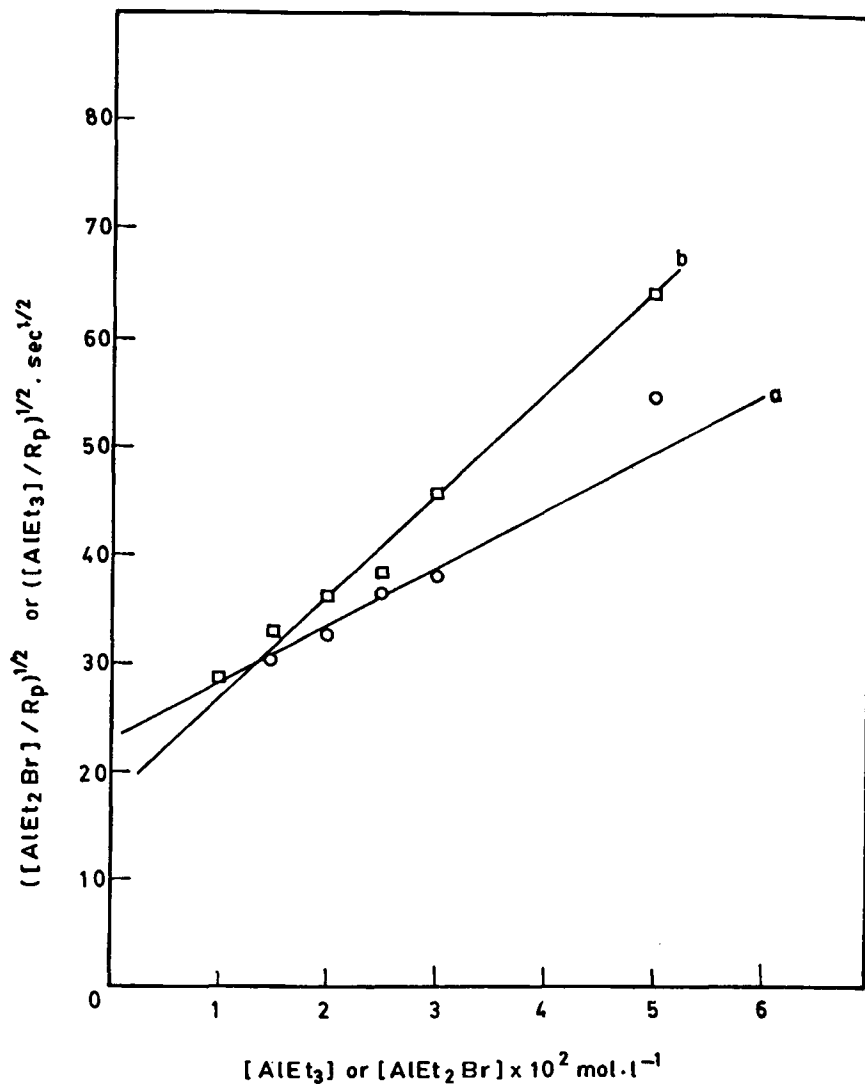


FIG. 6. The Langmuir-Hinshelwood plot for the polymerization of 1-octene with (a) catalyst I and (b) catalyst II.

TABLE 7. Effect of the Temperature on the Rate of Polymerization and the Molecular Weight of the Polymer^a

Temperature, T, °C	$10^3/T$ (°K ⁻¹)	$R_p \times 10^5 \text{ mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$		Log $R_p + 5$		Molecular weight $\times 10^{-4}$	
		Catalyst I	Catalyst II	Catalyst I	Catalyst II	Catalyst I	Catalyst II
35	3.247	1.8199	1.523	0.260	0.1827	9.151	7.286
40	3.200	1.9814	1.627	0.297	0.2110	8.711	7.136
45	3.145	2.9791	1.960	0.474	0.2920	7.380	6.940
50	3.096	3.1412	2.802	0.497	0.4475	6.020	5.573
55	3.049	4.3190	4.082	0.635	0.6109	4.954	4.381
60	3.003	5.3620	5.077	0.729	0.7056	3.429	3.196

^aPolymerization conditions as in Table 2.

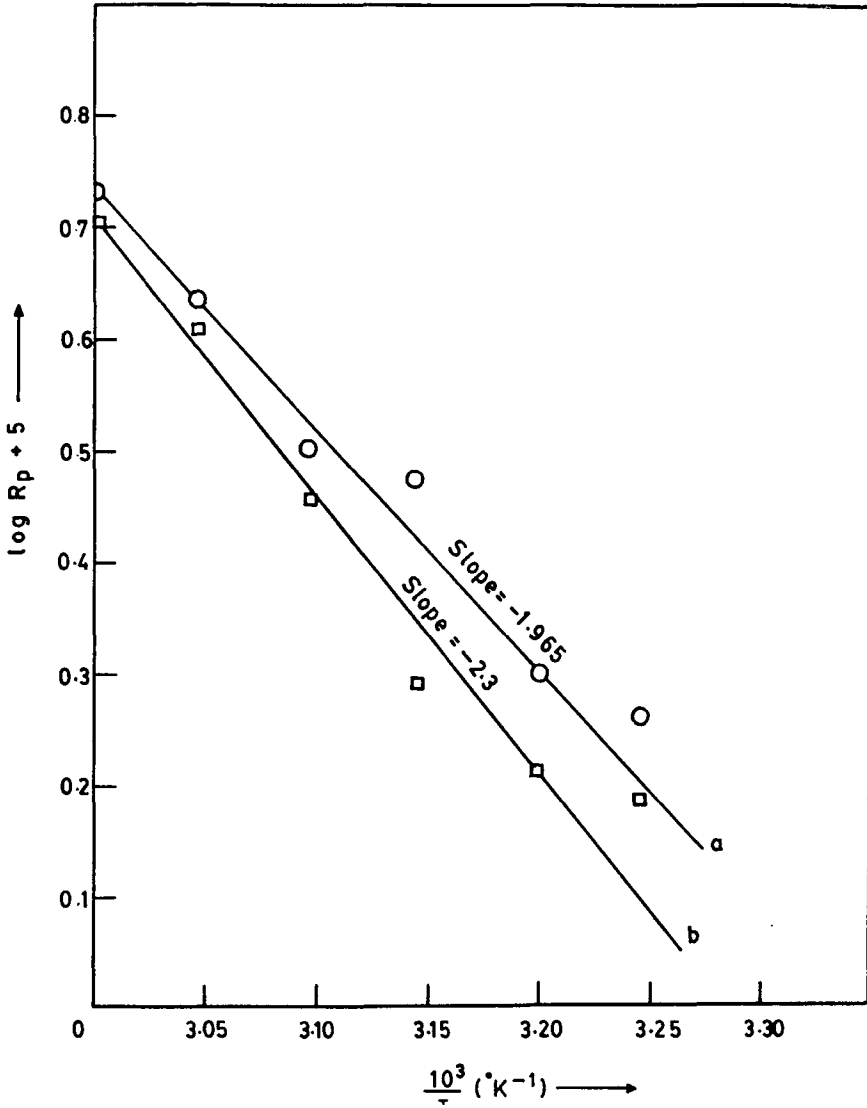


FIG. 7. Arrhenius plot for the polymerization of 1-octene with (a) catalyst I and (b) catalyst II.

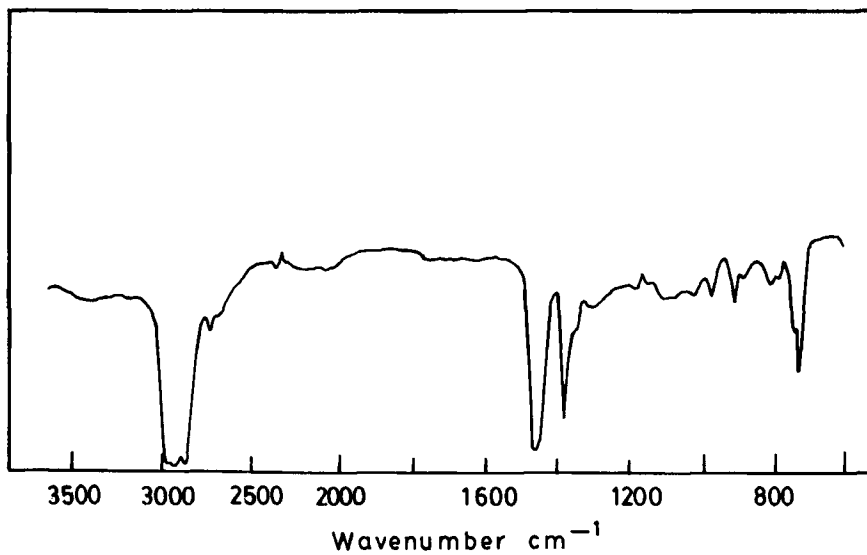
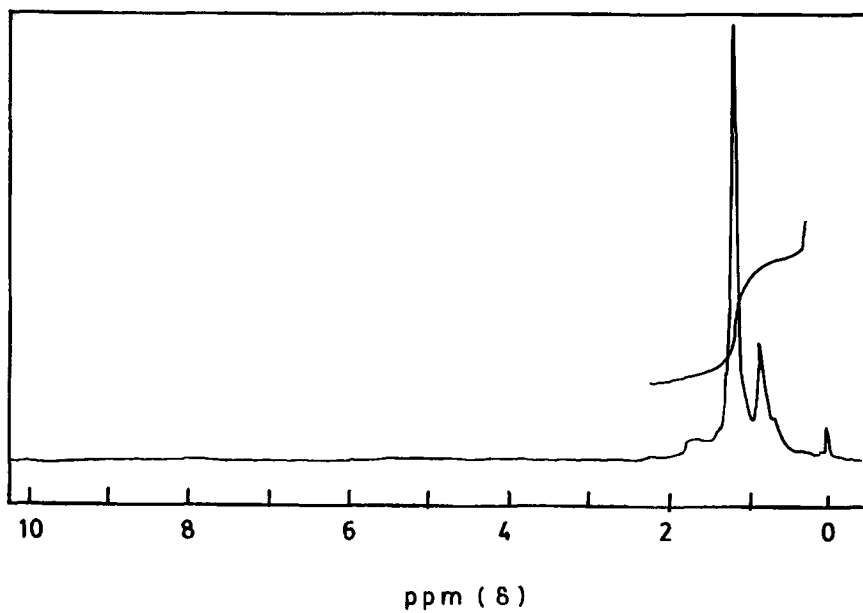


FIG. 8. IR spectrum of poly(1-octene).

FIG. 9. $^1\text{H-NMR}$ spectrum of poly(1-octene).

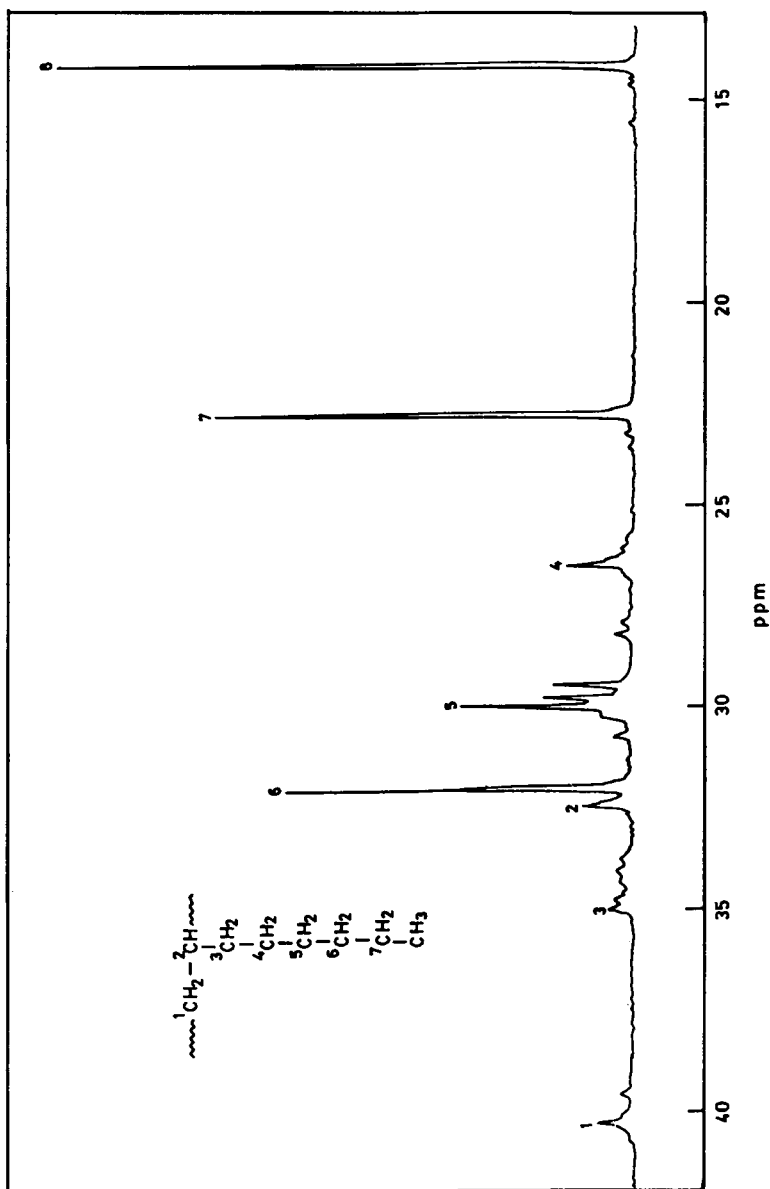


FIG. 10. ^1H -decoupled ^{13}C -NMR spectrum of poly(1-octene).

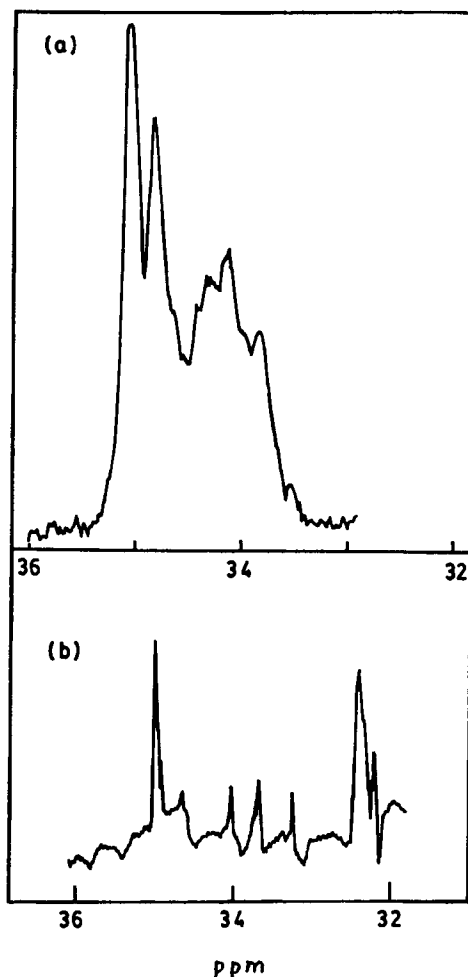


FIG. 11. ^{13}C -NMR spectra of the C^3 carbons of poly(1-octene) prepared with the polymerization of 1-octene with (a) catalyst I and (b) catalyst II.

CONCLUSIONS

From a study of the polymerization kinetics of 1-octene it was found that the rate of polymerization is first order with respect to both catalyst and monomer concentrations. The dependence of the rate of polymerization on the alkyl aluminum concentration is explained by a coordinate anionic mechanism involving competitive adsorption of both the monomer and the aluminum alkyl.

ACKNOWLEDGMENTS

We gratefully acknowledge Dr. N. Kalyanam (SPIC Pharmaceuticals, Madras) and Dr. T. Narasimhaswamy for helpful discussions. M.S.D. is grateful for a fellowship from CSIR.

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Received May 17, 1993